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MASS SPECTRAL STUDIES OF 1-(2-CHLOROETHOXY)-2-[(2-CHLOROETHYL)THIO] ETHANE AND RELATED COMPOUNDS USING GAS CHROMATOGRAPHY–MASS SPECTROMETRY AND GAS CHROMATOGRAPHY–TRIPLE- QUADRUPOLE MASS SPECTROMETRY

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The electron impact and collision-induced-dissociation mass spectra of 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane and 10 related molecules were obtained using gas chromatography–mass spectrometry and gas chromatography–triple-quadrupole mass spectrometry. These mass spectral studies were performed to facilitate the development of a spectral database of mustard-related compounds for verification purposes in support of the Chemical Weapons Convention. The proposed fragmentation pathways of the individual molecules are reported with rationalizations for the most characteristic ions.

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PREFACE

The work described in this report was started in October 2014 and completed in May 2015.

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1. INTRODUCTION

Since their introduction on the battlefield in World War I, sulfur mustards, bis(2-chloroethyl) sulfide and related compounds, have been some of the easiest chemical warfare agents to produce and store. In the years since World War I, each decade has seen many suspected and recorded uses of sulfur mustard,[1,2] from its use in the 1980s during the Iran–Iraq war to its persistently rumored use in present-day Syria. Mustard's utilization combined with its stockpiling in many countries, ease of production, and potential use by terrorists has resulted in renewed interest and research. A recent search of *Chemical Abstracts*[3] yielded about 900 English-language references to sulfur mustard in the last five years alone. Clearly, new information regarding mustard and mustard-related compounds is still relevant to the scientific community.

We previously synthesized 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane (also known as "little t"), a byproduct of sulfur mustard production that is found in ton storage containers, along with 10 related compounds (Figure 1).[4] The mass spectral identification of 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane (**4)** has appeared sporadically in the literature,[5–13] and we now report on the characterization of **4** and related structures using gas chromatography–mass spectrometry (GC–MS) and gas chromatography–triple-quadrupole mass spectrometry (GC–QQQ). The mass spectral studies reported herein were performed as part of an effort to facilitate the development of a spectral database of mustard compounds for verification and identification purposes in support of the Chemical Weapons Convention (CWC).[14]

The degradation of sulfur mustard in the environment and in storage is complex. The pathways and products of sulfur mustard degradation under a variety of field and laboratory conditions have been extensively described.[15–21] An analysis of sulfur mustard ton containers in the U.S. stockpile showed that byproducts were formed during manufacturing, and products were formed from slow condensation reactions within the storage container.[20] Identification of these other mustard-related products with GC–MS was difficult because of their similarity, their lack of unique and easily distinguishable functional groups, and (often) the absence of a molecular ion. Although the topic of sulfur mustard is well represented in the literature, not much information exists pertaining to the mass spectral analysis of polyacyclic halogenated ethers or thioethers, molecules that could be considered part of the sulfur mustard family. The bulk of the work on these types of molecules has focused on analysis of mixtures obtained from environmental samples or simulated environmental conditions. Other than **4**, which was reported on previously, this is the first report of a mass spectral study of authentic (synthesized) samples of this type; therefore, this work is of interest to the CWC community.

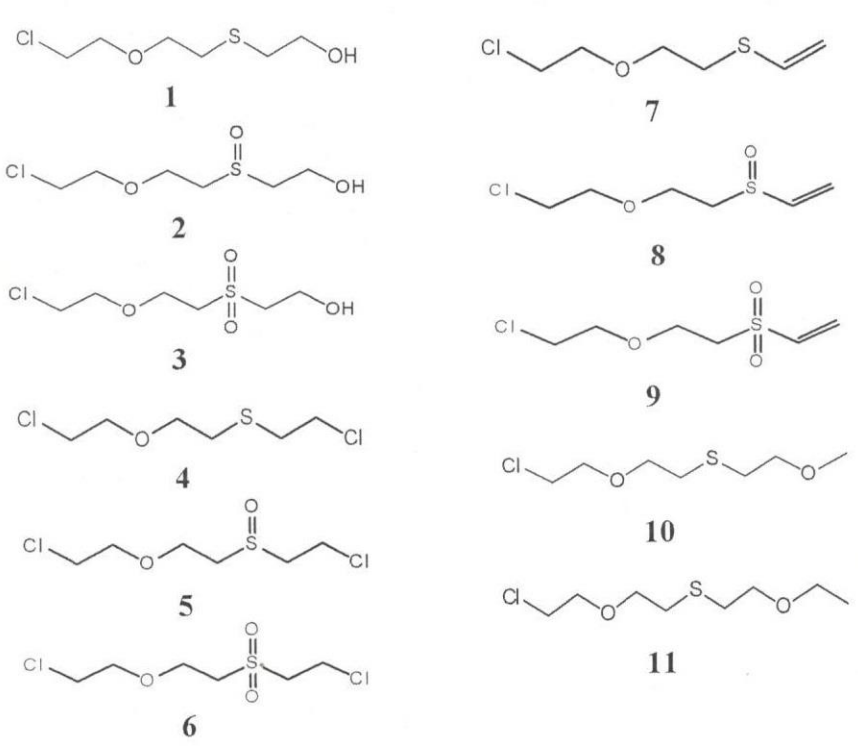


Figure 1. Molecular structures of compounds **1**–**11**.

2. EXPERIMENTAL METHODS

Compounds **1–11** (Figure 1) were synthesized at the U.S. Army Edgewood Chemical Biological Center (Aberdeen Proving Ground, MD) in accordance with previously published procedures.[4] Analytical grade dichloromethane (CH_2Cl_2, >99.8% purity) was obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO) and was used as received. Each sample (1 mg/mL) was prepared in analytical grade CH_2Cl_2.

The GC–MS analyses of compounds **1–11** were performed on an Agilent 5975 mass spectrometer interfaced to an Agilent 6890 gas chromatograph (Agilent Technologies; Santa Clara, CA). The GC was equipped with an Agilent J&W Scientific HP-5ms bonded-phase capillary column (30 m × 0.25 mm i.d.) with a film thickness of 0.25 µm. The injection port temperature was 220 °C, the GC–MS interface temperature was 250 °C, and the source temperature was 150 °C. The carrier gas was helium, with a flow rate of 1 mL/min, and the oven temperature was programmed from 60 to 250 °C at 15 °C/min. A split injector was used (split ratio, 75:1), and a 0.2 µL volume of sample was placed on the column. The scanned mass range was 50 to 450 Da at 4 scans/s.

The gas chromatography–tandem mass spectrometry (GC–MS-MS) analysis was performed on an Agilent 7000 GC–QQQ mass spectrometer interfaced to an Agilent 7890A gas chromatograph. The instrument was equipped with a 30 m × 0.25 mm i.d. HP-5ms capillary column with a film thickness of 1.0 µm. The injector port temperature was 250 °C, the GC–MS interface temperature was 250 °C, and the source temperature was 150 °C. The carrier gas was

helium, with a flow rate of 1.2 mL/min, and the oven temperature was programmed from 60 to 250 °C at 15 °C/min. A split injector was used (split ratio, 10:1), and a 1.0 µL volume of sample was placed on the column. Nitrogen was used as the collision gas for the collision-induced dissociation (CID). The pressure in the collision cell was 1.5 mT, and the collision energy was –15 eV. The scanned mass range was 20 to 200 Da at 1 scan/s. Qualitative and quantitative analyses were processed using MassHunter software (Agilent Technologies), which was supplied with the MS data system.

3. RESULTS AND DISCUSSION

An electron impact (EI) mass spectrum often contains the molecular ion, $M^{+\bullet}$, but because of the presence of one or two chlorine atoms in molecules **1–11**, the molecular ions in 9 of the 11 molecules were either extremely small or essentially nonexistent and undetectable. Because of this, the fragmentation pattern was the main tool used for unknown identification and characterization. Triple-quadrupole analyzers allow for a selectivity improvement by minimizing interferences, and they enhance sensitivity by providing access to adequate precursor and product ion selections.[22,23] EI and CID spectra were obtained for all 11 compounds under the general conditions described in Section 2.

The 11 molecules shown in Figure 1 were analyzed using GC–MS and GC–QQQ. A mass ion of interest was selected for each individual compound, and the relative percent abundances of the fragment ions were calculated for the EI and CID results (Table 1).

Table 1. Compounds Identified by GC–MS and GC–MS-MS Analyses, Including Fragment Ions and Relative Percent Abundances

Compound No.	MW	Mass Spectral Data (% relative abundance)	
		EI	CID
1	184	61 (90.3), 63 (58.2), 75 (28.0), 91 (14.2), 105 (100), 148 (1.7)	MS2 *m/z* 105: 45 (100), 61 (42), 87 (13.3), 105 (51.2)
2	200	63 (100), 76 (20.8), 94 (9.6), 107 (16.1), 128 (5.7)	MS2 *m/z* 107: 45 (11.7), 63 (100), 107 (9.7)
3	216	63 (100), 72 (18.1), 93 (9.8), 109 (35.2), 137 (57.2), 167(14.2)	MS2 *m/z* 137: 45 (100), 93 (7.6), 109 (40.1), 137 (50.4) MS2 *m/z* 167: 45 (14.9), 109 (33.5), 137 (100), 167 (23.4)
4	202	63 (87.8), 93 (21.4), 109 (24.1), 123 (100), 166 (10.5)	MS2 *m/z* 123: 61 (23.6), 63 (100), 95 (12.8), 123 (80.8)
5	218	63 (100), 76 (10.9), 107 (13.0), 128 (3.1)	MS2 *m/z* 107: 45 (11.6), 63 (100), 107 (9.0)
6	234	63 (100), 106 (16.8), 155 (30.8), 185 (9.4)	MS2 *m/z* 155: 63 (100), 93 (8.0), 127 (24.4), 155 (40.5) MS2 *m/z* 185: 63 (24.6), 127 (25.9), 155 (100), 185 (17.7)
7	166	63 (100), 73 (59.2), 87 (79.1), 106 (23.3), 166 (19.0)	MS2 *m/z* 166: 43 (68.2), 63 (29.4), 120 (83.9), 131 (2.6), 166 (8.2)
8	182	63 (100), 76 (25.6), 107 (18.4)	MS2 *m/z* 107: 45 (11.8), 63 (100), 107 (9.5)
9	198	63 (95.7), 91 (100), 106 (32.9), 119 (71.2), 149 (35.8)	MS2 *m/z* 149: 27 (4.9), 91 (100), 119 (98.6), 149 (18.9)
10	198	59 (77.3), 63 (60.5), 75 (79.2), 103 (20.6), 119 (100)	MS2 *m/z* 119: 59 (100), 87 (10.9), 119 (43.5)
11	212	59 (100), 75 (95.4), 88 (21.7), 103 (25.0), 133 (84.4)	MS2 *m/z* 133: 45 (97.5), 73 (100), 87 (6.7), 105 (5.9), 133 (25.6)

The EI mass spectrum for compound **1** exhibited an extremely small to undetectable molecular ion at *m/z* 184 and an isotopic ion at *m/z* 186 due to chlorine. Other mass ions due to $[M–HCl]^+$, $[M–OCH_2CH_2Cl]^+$, and $[M–OC_3H_6Cl]^+$ were observed at *m/z* 148, *m/z* 105, and *m/z* 91, respectively (Figure 2a). The mass ion at *m/z* 105 was selected for CID and produced three major ions with *m/z* values of 87, 61, and 45, with a relative intensity ratio of 13:42:100. The *m/z* 87 ion was due to loss of H_2O, the *m/z* 61 ion was due to loss of C_2H_4O, and the *m/z* 45 ion was due to loss of CH_2CH_2S (Figure 2b). The proposed fragmentation pathway is shown in Scheme 1.

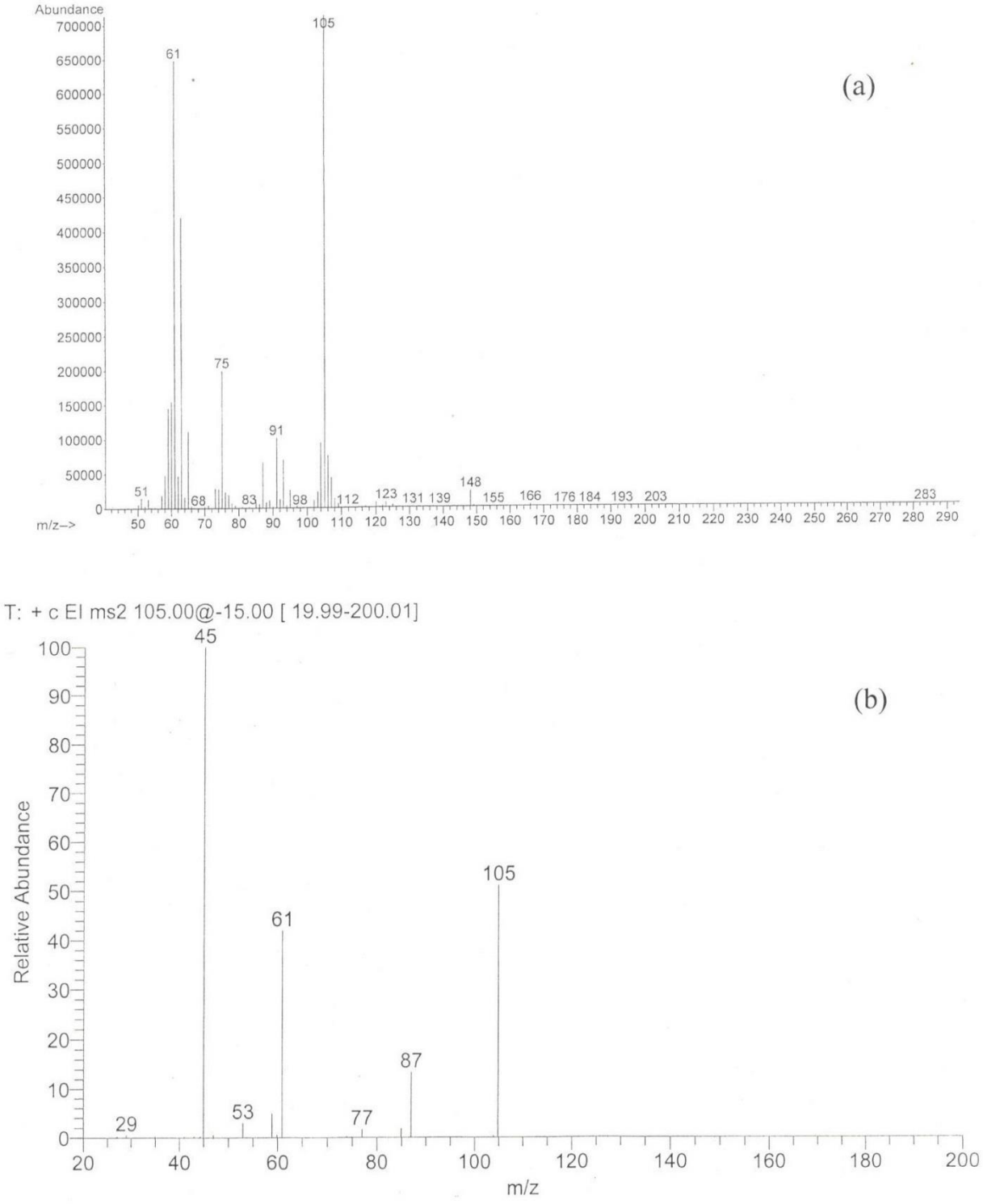
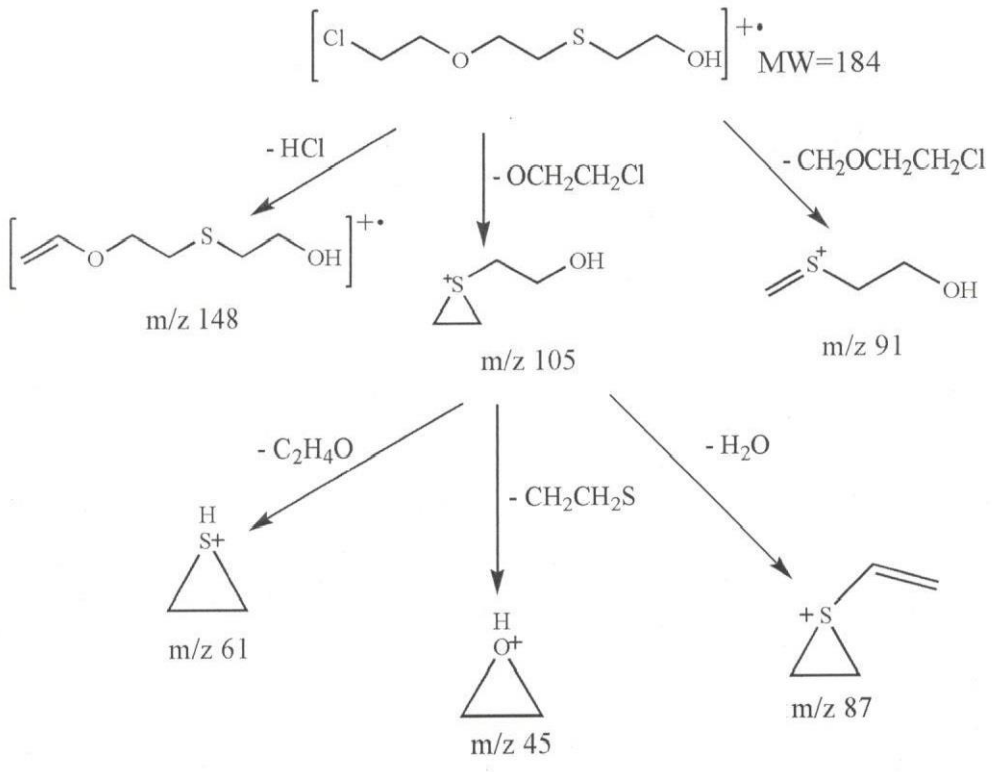
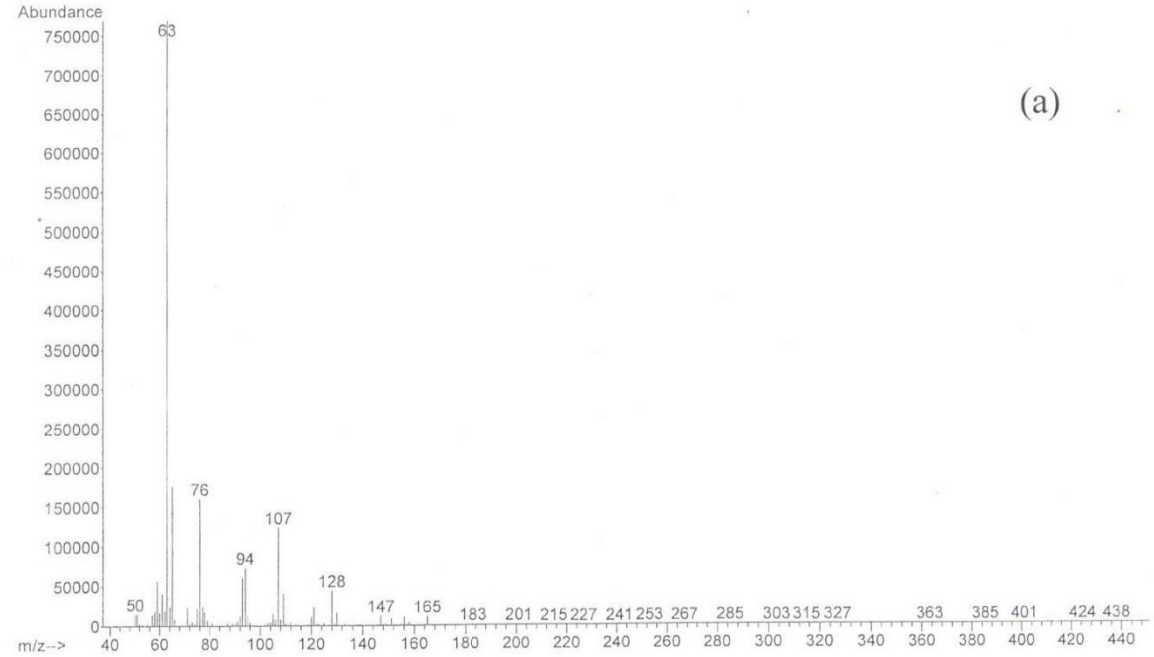


Figure 2. Mass spectra for compound **1**: (a) EI and (b) CID at *m/z* 105.



Scheme 1. Proposed fragmentation pathway for compound **1**.

The EI mass spectrum for compound **2** contained an extremely small molecular ion at *m/z* 200 and an isotopic ion at *m/z* 202. Other mass ions due to $[M–HCl]^+$, $[M–C_2H_5SO_2]^+$, and $[M–OC_5H_9Cl]^+$ were observed at *m/z* 165, *m/z* 107, and *m/z* 94, respectively. The lower mass ion at *m/z* 63 was due to loss of $C_4H_9SO_3$ (Figure 3a). The mass ion at *m/z* 107 was selected for CID and produced two major ions at *m/z* 63 and *m/z* 45, due to $[C_2H_4Cl]^+$ and $[C_2H_5O]^+$, respectively, with a relative intensity ratio of 100:12 (Figure 3b). The proposed fragmentation pathway is illustrated in Scheme 2.



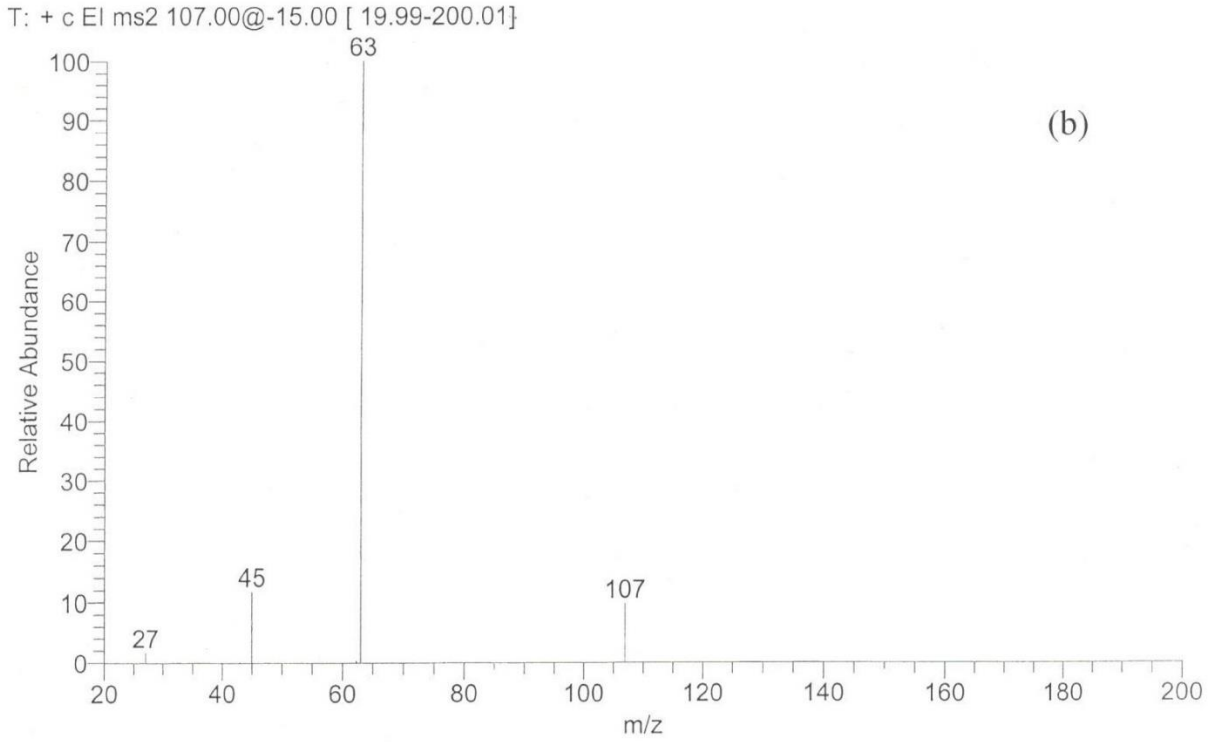
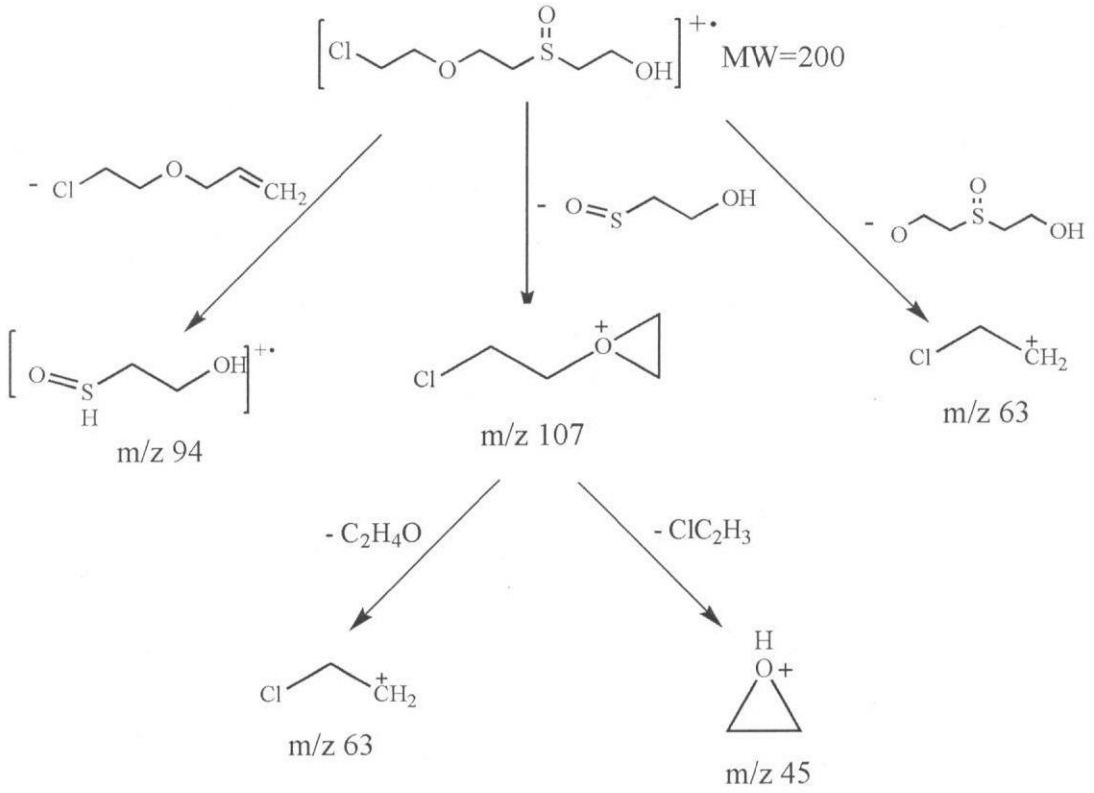


Figure 3. Mass spectra for compound **2**: (a) EI and (b) CID at *m/z* 107.



Scheme 2. Proposed fragmentation pathway for compound **2**.

The EI mass spectrum for compound **3** showed six principal ions with *m/z* values of 167, 137, 109, 93, 79, and 63 (Figure 4a). No molecular ion was observed. Mass ions at *m/z* 167 and *m/z* 109 were formed due to $[M\text{-}CH_2Cl]^+$ and $[M\text{-}CH_2CH_2OCH_2CH_2Cl]^+$, respectively. Two EI fragments (*m/z* 137 and *m/z* 167) were selected for CID. Three product ions at *m/z* 93, *m/z* 109, and *m/z* 119 due to $[C_4H_7SO_2]^+$, $[C_2H_5SO_3]^+$, and $[C_2H_5SO_2]^+$, respectively, with a relative intensity ratio of 8:40:1, were observed in the CID spectrum for *m/z* 137 (Figure 4b). The CID for *m/z* 167 contained three major ions with *m/z* values of 45 (loss of $C_3H_6SO_3$), 109 (loss of C_3H_6O), and 137 (loss of CH_2O), with a relative intensity ratio of 15:34:100 (Figure 4c). The proposed fragmentation pathway is illustrated in Scheme 3.

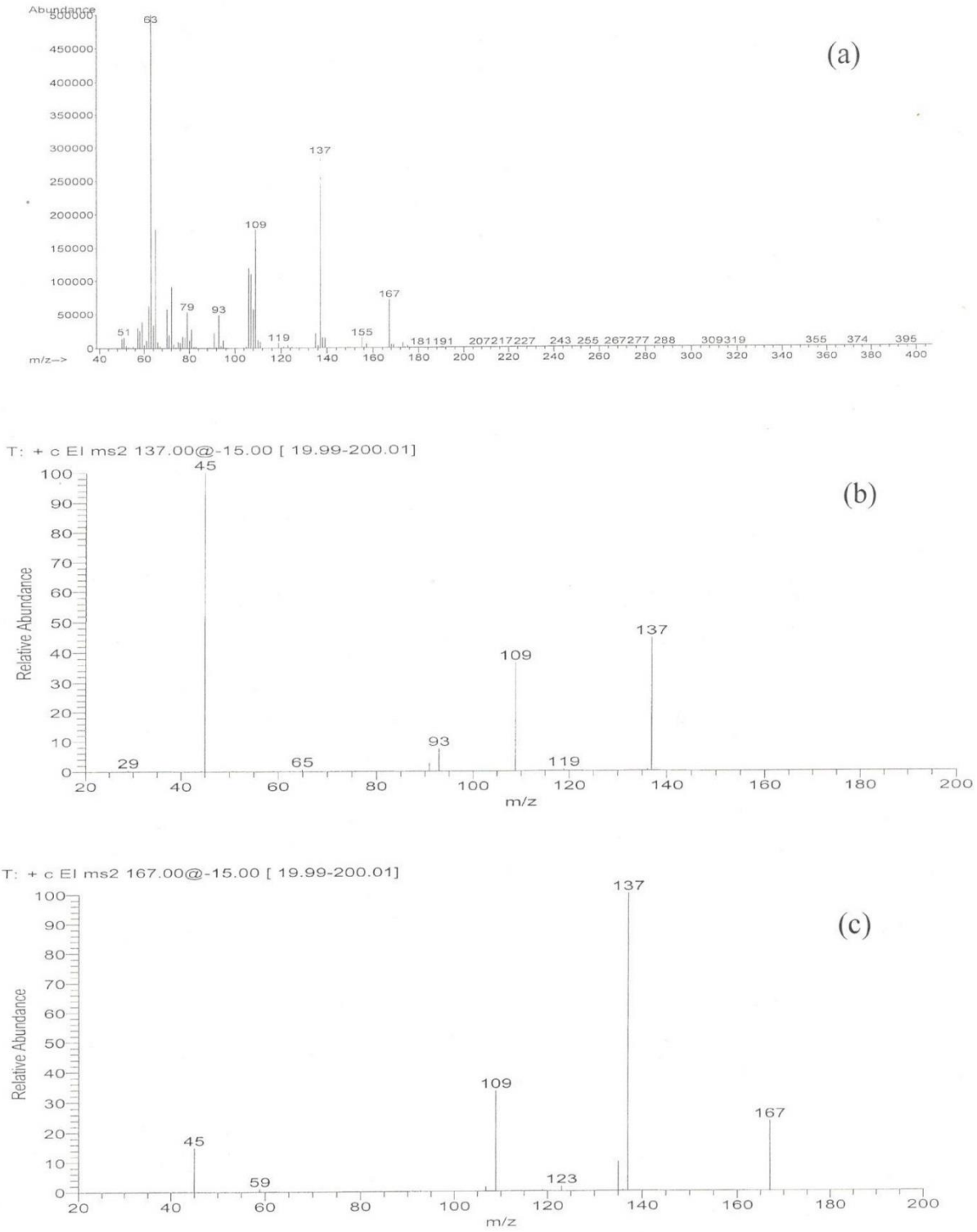
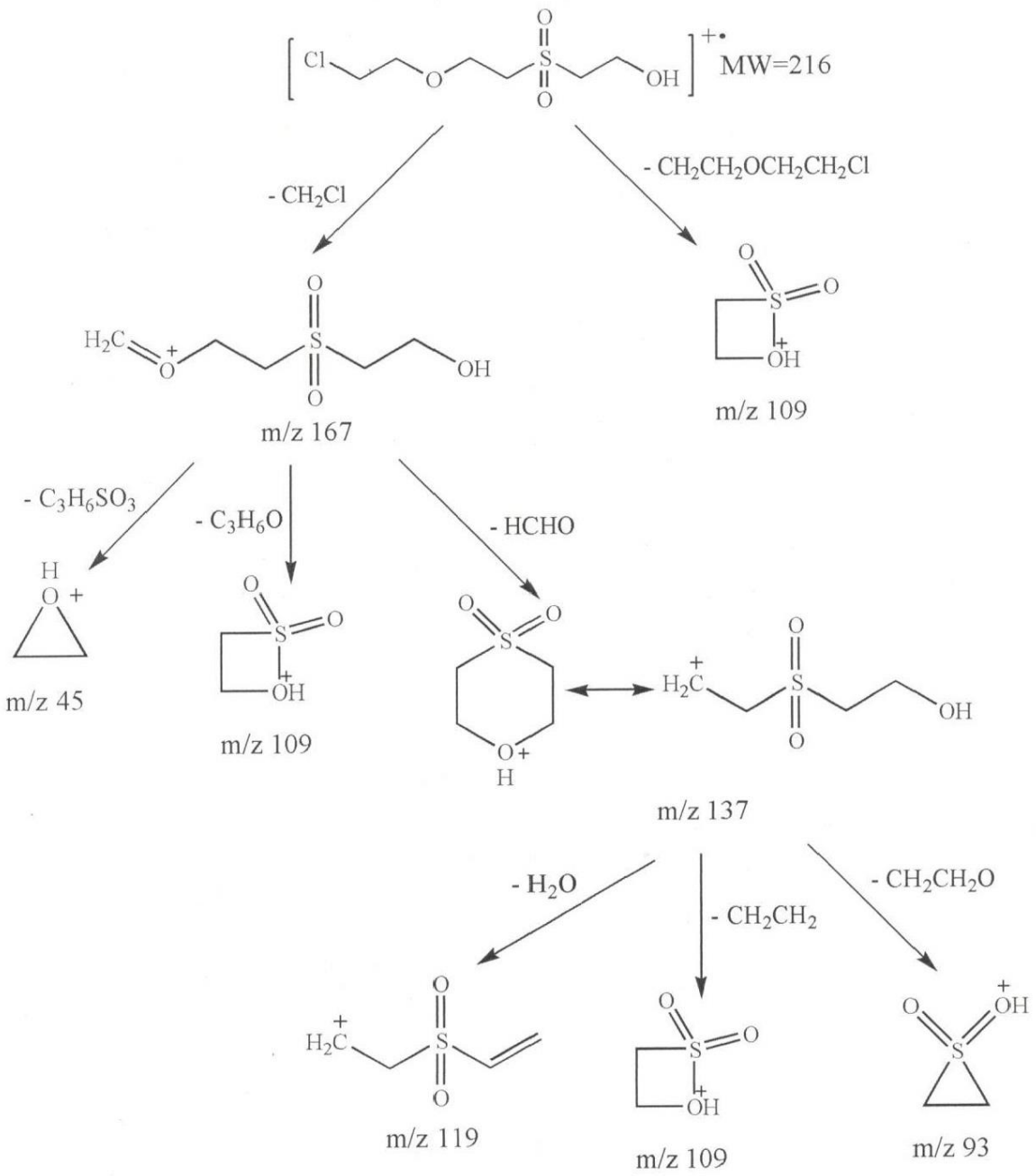


Figure 4. Mass spectrum for compound **3**: (a) EI, (b) CID at *m/z* 137, and (c) CID at *m/z* 167.



Scheme 3. Proposed fragmentation pathway for compound **3**.

The EI mass spectrum for compound **4** contained an extremely small to undetectable molecular ion at *m/z* 202 and isotopic ions at *m/z* 204 and *m/z* 206. Other mass ions due to $[M–HCl]^+$, $[M–OCH_2CH_2Cl]^+$, and $[M–CH_2SCH_2CH_2Cl]^+$ were observed at *m/z* 166, *m/z* 123, and *m/z* 93 (Figure 5a). The mass ion at *m/z* 123 was selected for CID and produced three major ions at *m/z* 63, *m/z* 87, and *m/z* 95 due to $[C_2H_4Cl]^+$, $[C_4H_7S]^+$, and $[C_2H_4SCl]^+$, respectively, with a relative intensity ratio of 100:1:13 (Figure 5b). The proposed fragmentation pathway is illustrated in Scheme 4.

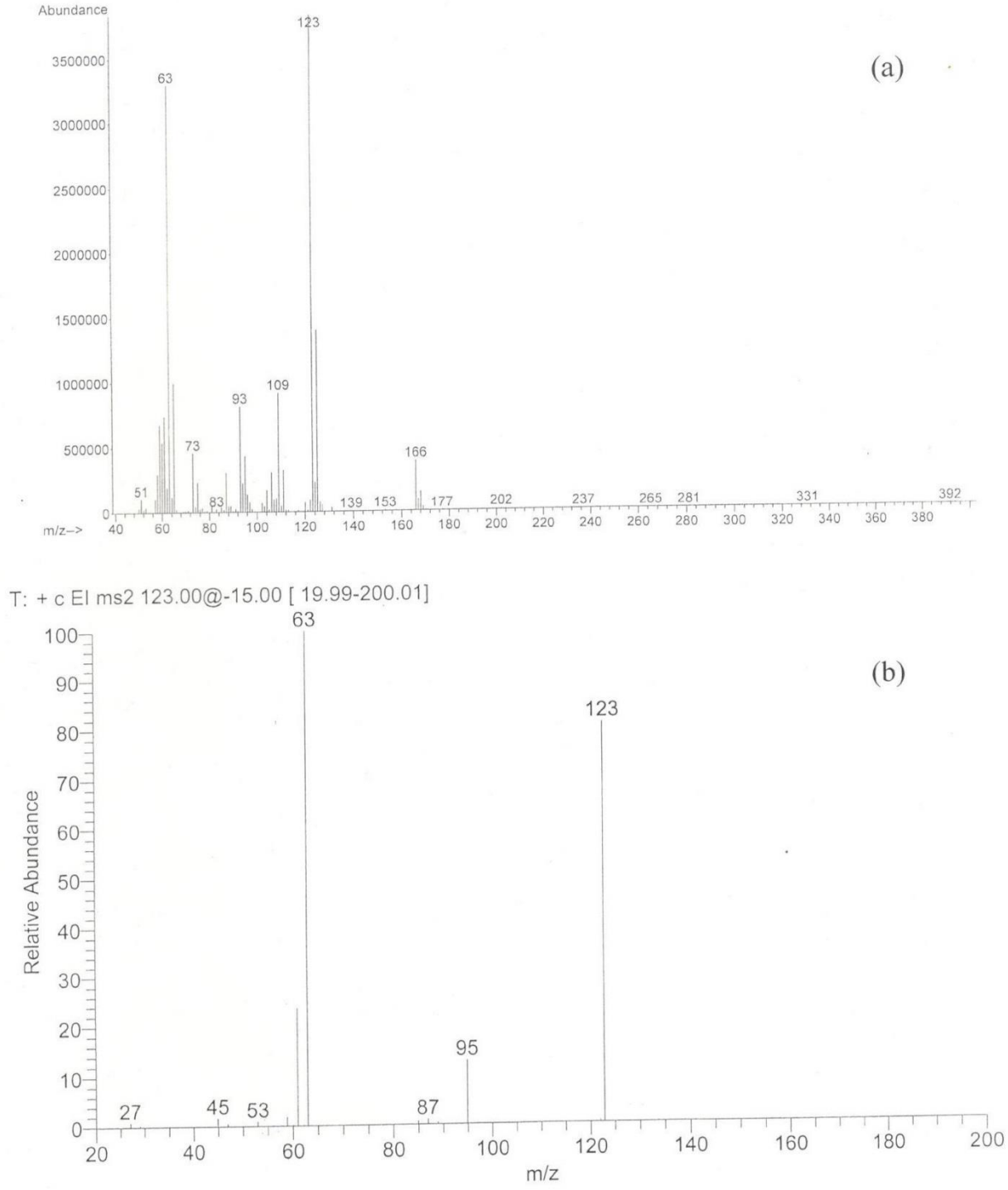
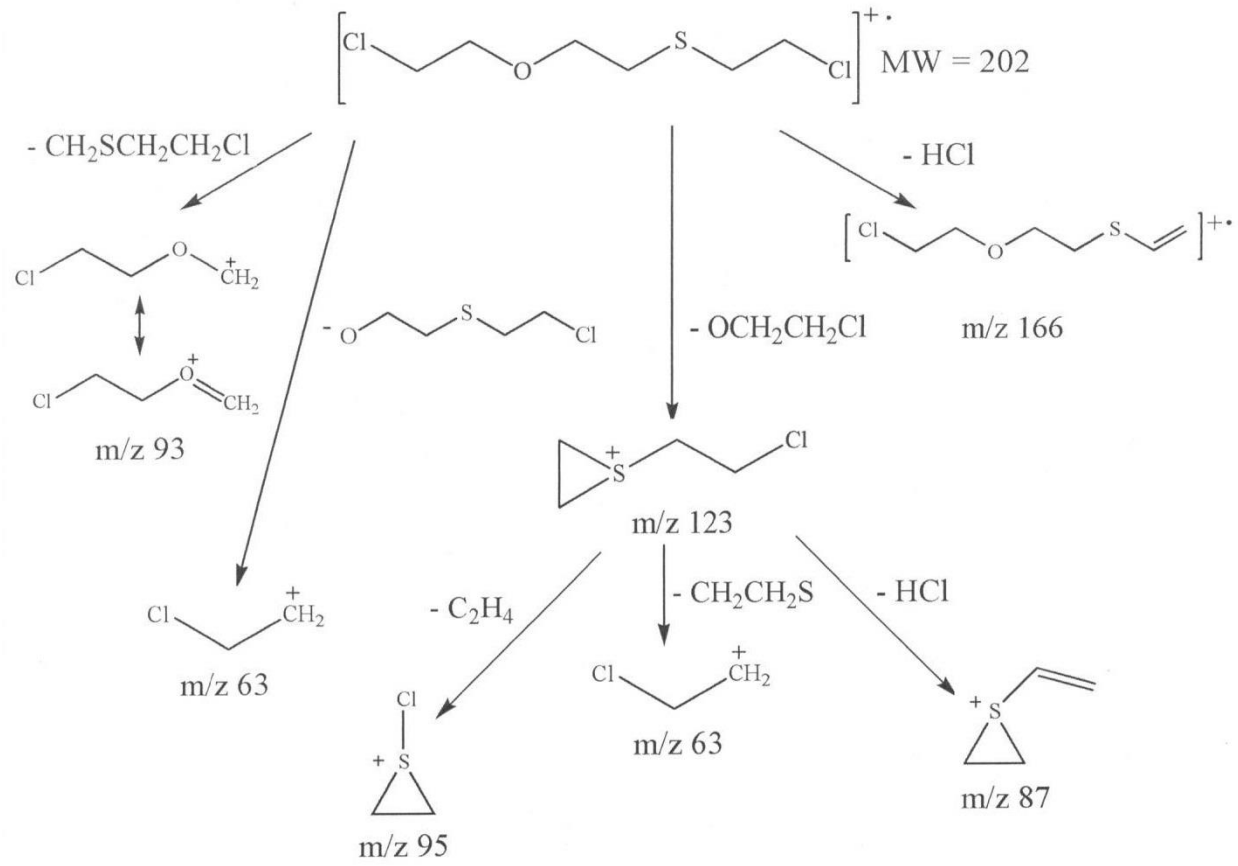


Figure 5. Mass spectra for compound **4**: (a) EI and (b) CID at *m/z* 123.



Scheme 4. Proposed fragmentation pathway for compound **4**.

The EI mass spectrum for compound **5** showed three principal ions with *m/z* values of 107, 76, and 63 (Figure 6a). No molecular ion was observed. The mass ion at *m/z* 107 was formed due to $[M–C_2H_4OSCl]^+$, and the lower mass ion at *m/z* 63 was from the loss of $C_4H_8SO_2Cl$. The mass ion at *m/z* 107 was selected for CID and produced two major ions with *m/z* 63 due to $[ClCH_2CH_2]^+$ and *m/z* 45 due to $[C_2H_5O]^+$ with a relative intensity ratio of 100:12 (Figure 6b). The proposed fragmentation pathway is illustrated in Scheme 5.

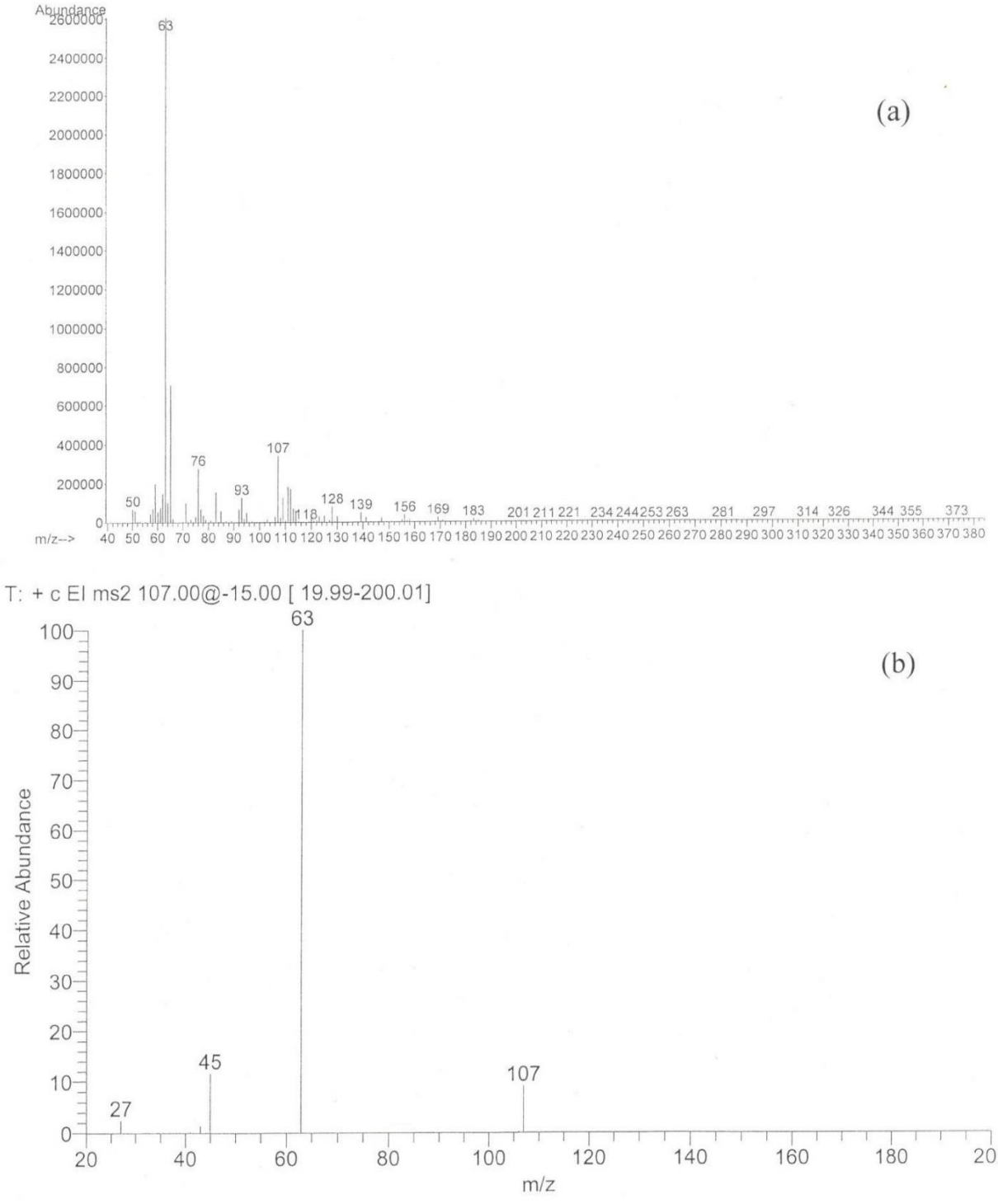
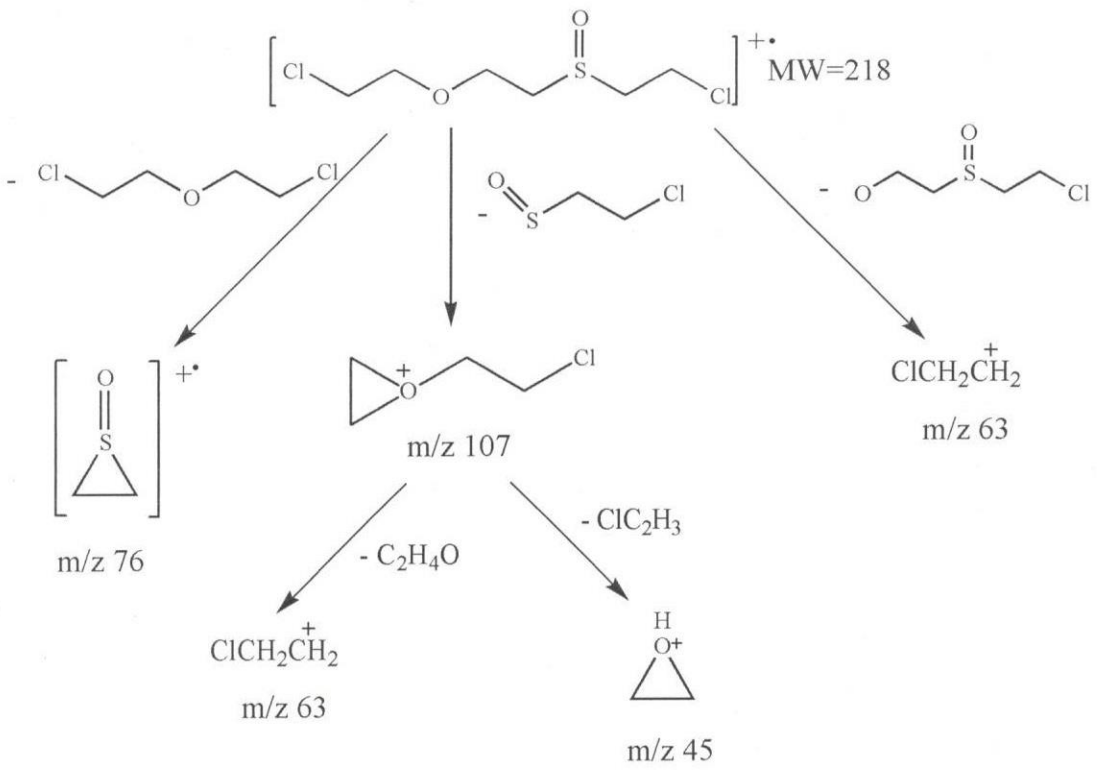


Figure 6. Mass spectra for compound **5**: (a) EI and (b) CID at *m/z* 107.



Scheme 5. Proposed fragmentation pathway for compound **5**.

The EI mass spectrum for compound **6** showed five principal ions with *m/z* values of 185, 155, 127, 106, and 63 (Figure 7a). The molecular ion was not observed. Mass ions at *m/z* 155 and *m/z* 185 were formed due to $[M–C_2H_5OCl]^+$ and $[M–CH_2Cl]^+$, respectively. Two mass EI fragmentation ions (*m/z* 155 and *m/z* 185) were selected for CID. Three product ions at *m/z* 63, *m/z* 93, and *m/z* 127, due to $[ClCH_2CH_2]^+$, $[C_2H_5SO_2]^+$, and $[C_2H_4SO_2Cl]^+$, respectively, with a relative intensity ratio of 100:8:24, were observed in the CID spectrum for the *m/z* 155 ion (Figure 7b). The CID for the *m/z* 185 ion contained three major ions with *m/z* values of 63 (due to loss of $C_3H_6SO_3$), 127 (due to loss of C_3H_6O), and 155 (due to loss of CH_2O), with a relative intensity ratio of 25:26:100 (Figure 7c). The proposed fragmentation pathway is illustrated in Scheme 6.

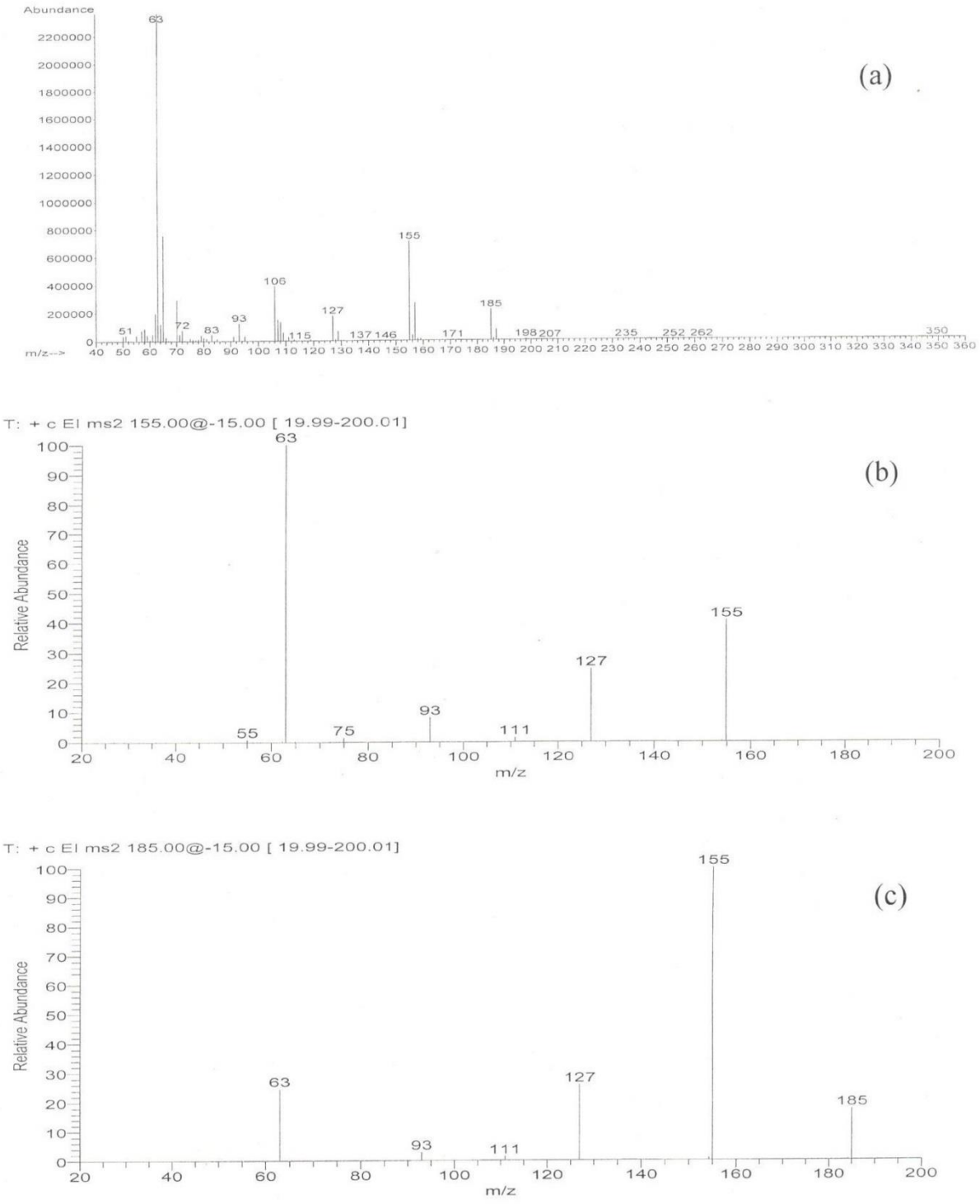
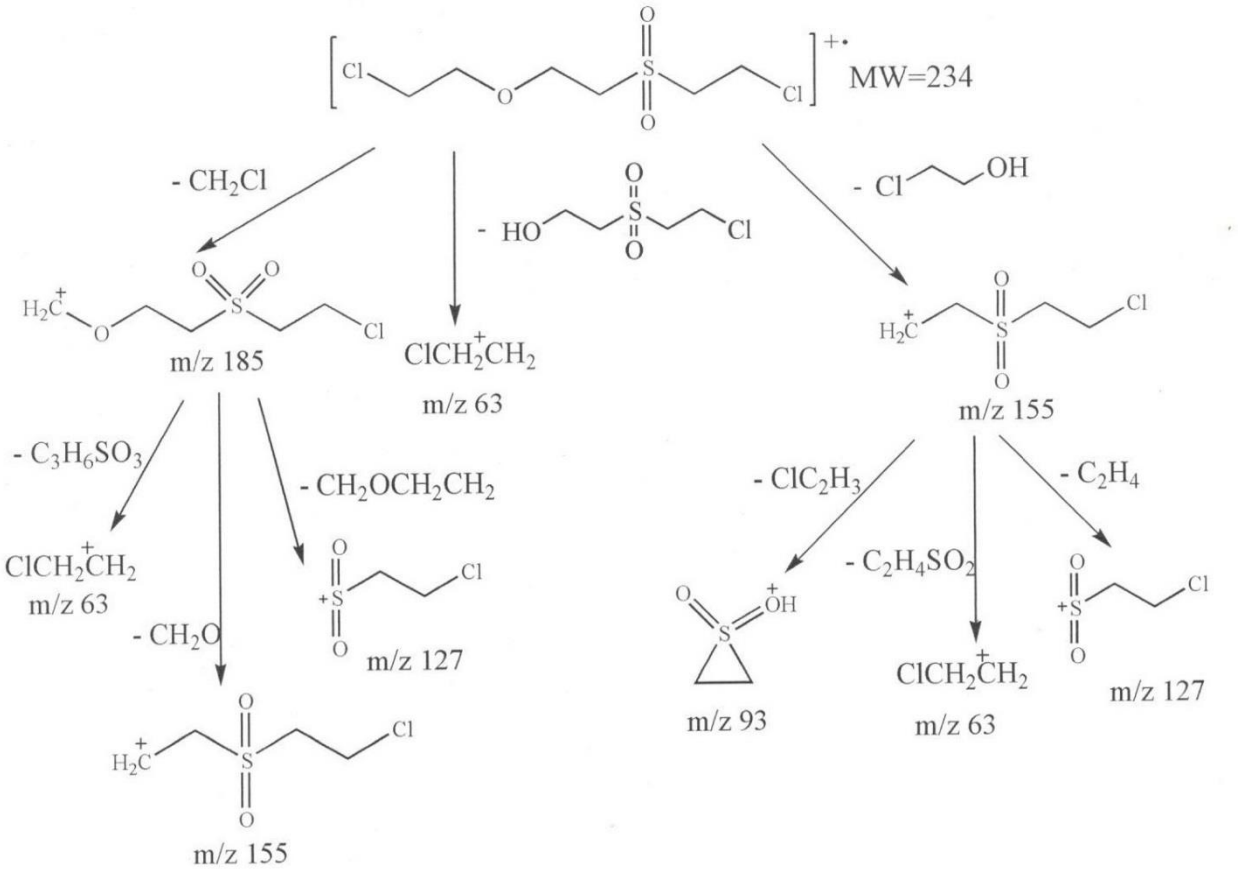


Figure 7. Mass spectra for compound **6**: (a) EI, (b) CID at *m/z* 155, and (c) CID at *m/z* 185.



Scheme 6. Proposed fragmentation pathway for compound **6**.

The EI mass spectrum for compound **7** contained a very large molecular ion at *m/z* 166 and an isotopic ion at *m/z* 168. Other mass ions at *m/z* 131 and *m/z* 106 were formed due to $[M–Cl]^+$ and $[M–C_3H_4S]^+$ (Figure 8a). Three potential resonance structures exist from the loss of chlorine from the molecular ion. The lower mass ions at *m/z* 63 (due to loss of C_4H_7SO) and *m/z* 43 (due to loss of CH_2CH_2Cl) are shown in Figure 8b. The CID spectrum for the mass ion at *m/z* 166 depicts three product ions with *m/z* values of 43, 63, and 131, with a relative intensity ratio of 68:29:3. The proposed fragmentation pathway is illustrated in Scheme 7.

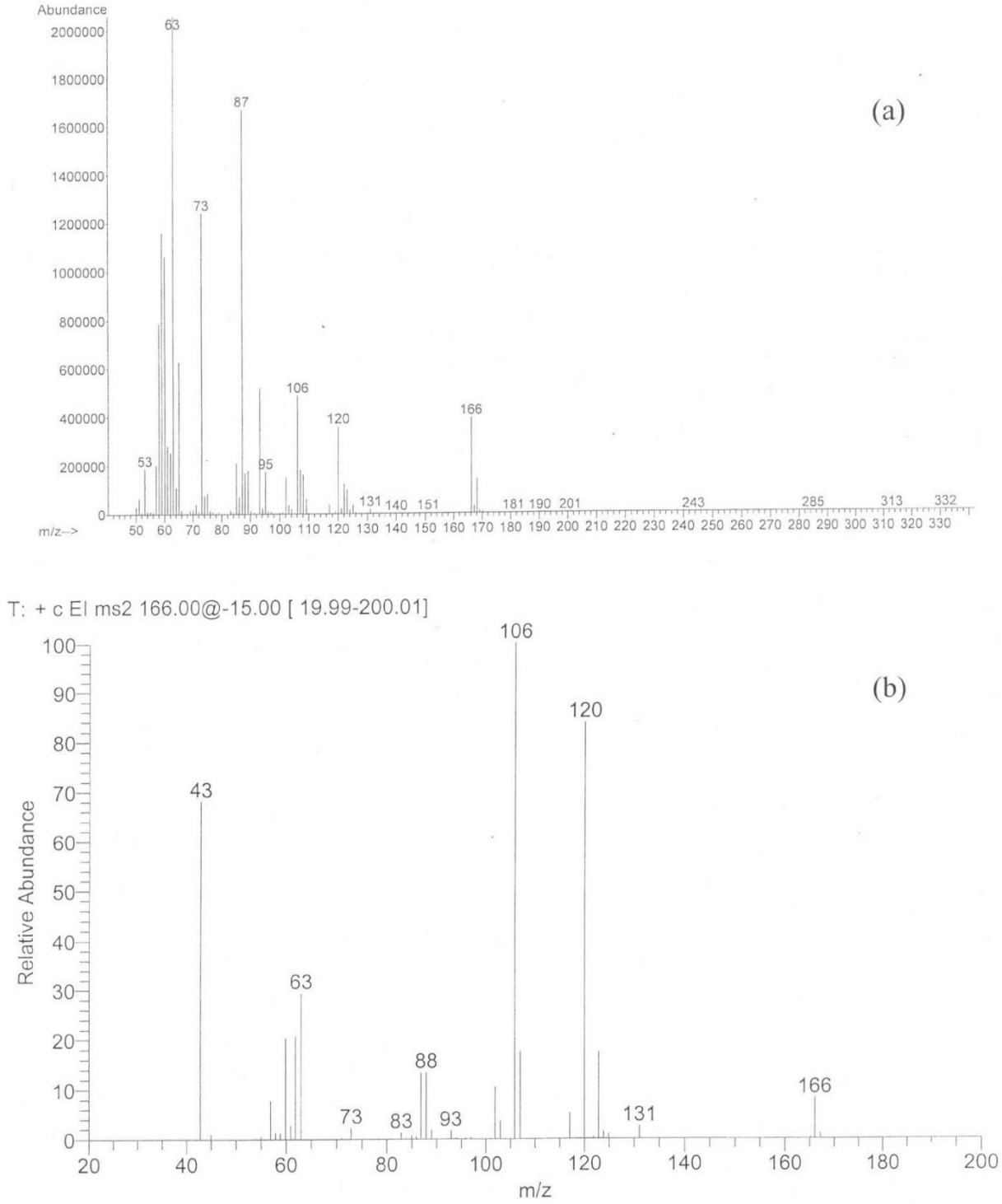
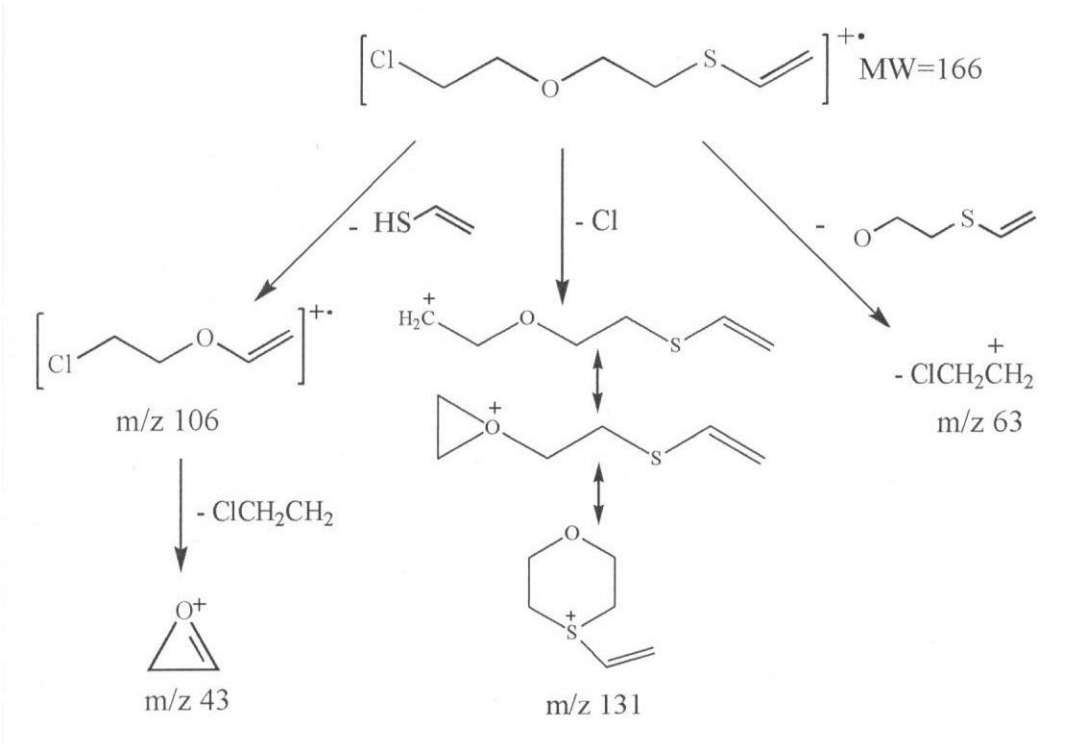


Figure 8. Mass spectra for compound **7**: (a) EI and (b) CID at *m/z* 166.



Scheme 7. Proposed fragmentation pathway for compound **7**.

The EI mass spectrum for compound **8** contained a small yet observable molecular ion at *m/z* 182 and an isotopic ion *m/z* 184. The mass ion due to $[M–C_4H_8OCl]^+$ at *m/z* 107 (Figure 9a) was selected for CID and contained two major ions at *m/z* 45 and *m/z* 63 due to $[C_2H_5O]^+$ and $[CH_2CH_2Cl]^+$, respectively, with a relative intensity ratio of 12:100 (Figure 9b). The proposed fragmentation pathway is illustrated in Scheme 8.

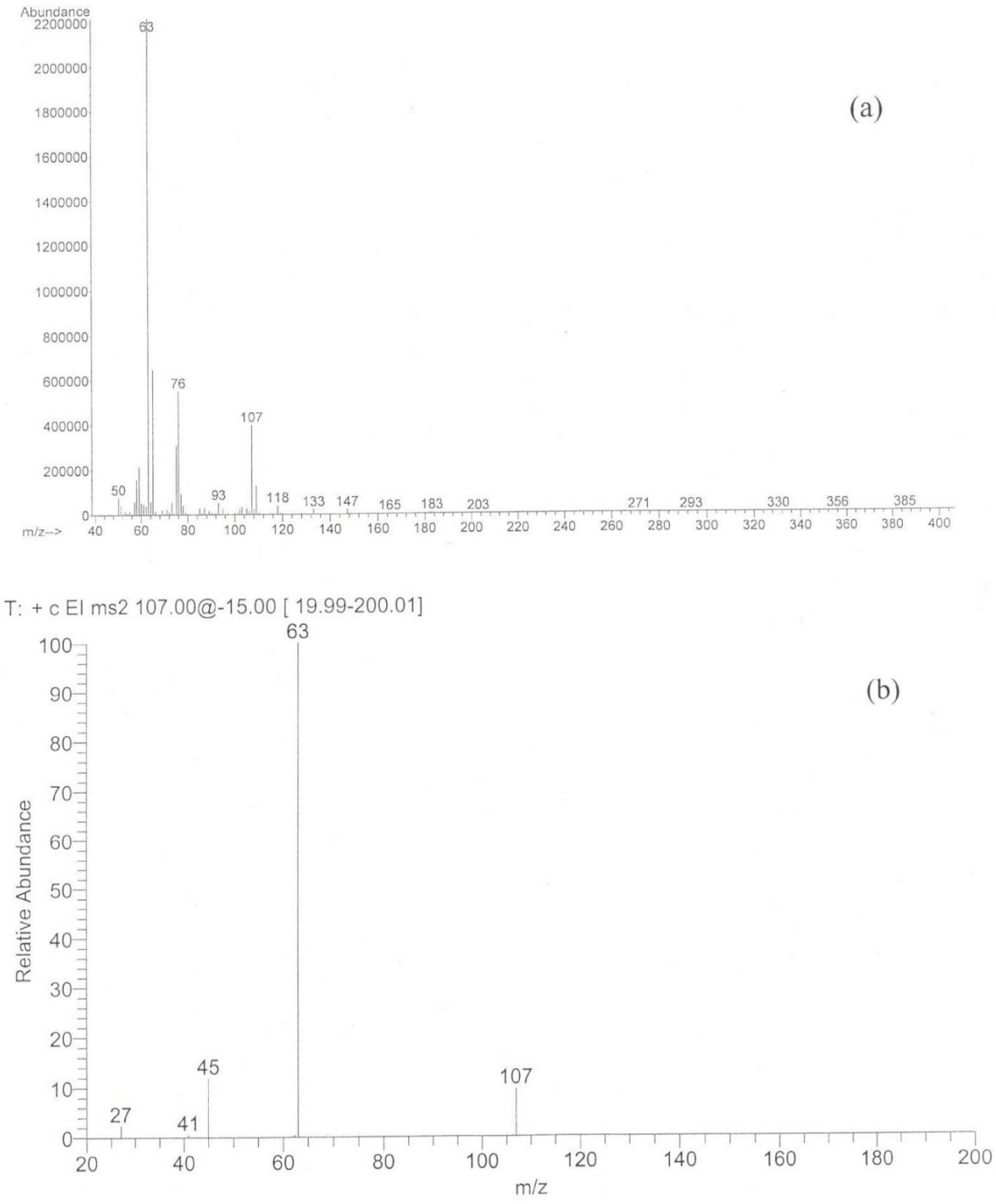
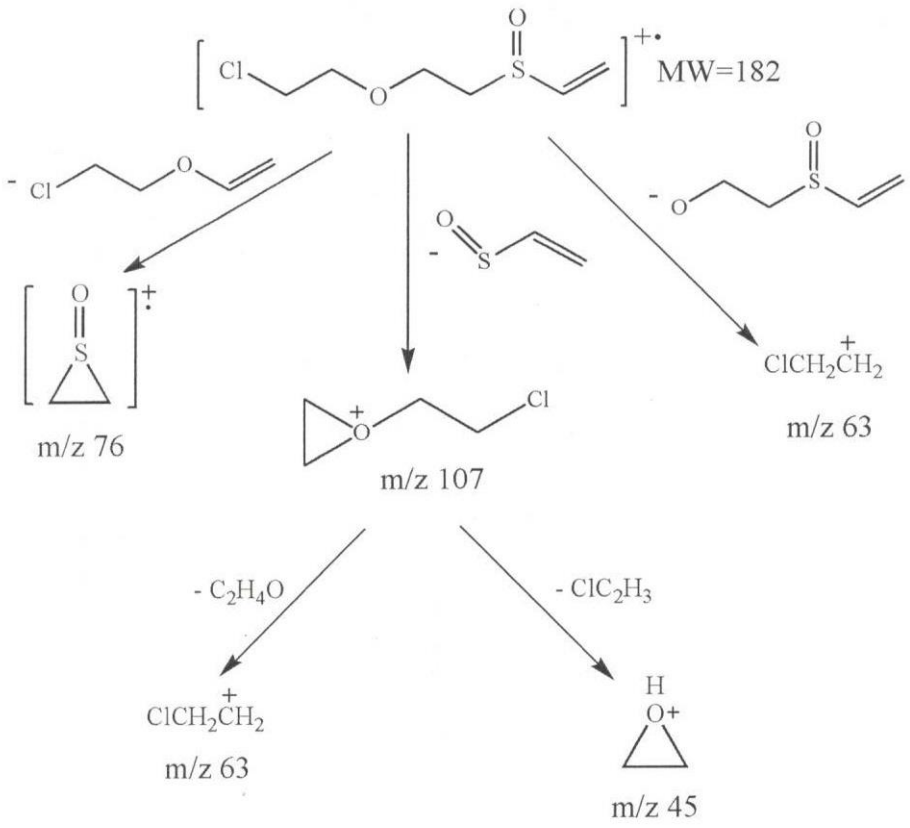


Figure 9. Mass spectra for compound **8**: (a) EI and (b) CID at *m/z* 107.



Scheme 8. Proposed fragmentation pathway for compound **8**.

The EI mass spectrum for compound **9** showed four principal ions with *m/z* values of 63, 91, 106, and 149. No molecular ion was detected at *m/z* 198. Mass ions at *m/z* 149 and *m/z* 106 were formed due to $[M–CH_2Cl]^+$ and $[M–C_2H_4SO_2]^+$, respectively. Lower mass ions at *m/z* 63 and *m/z* 91 were formed due to $[M–C_4H_7SO_3]^+$ and $[M–C_4H_8OCl]^+$, respectively (Figure 10a). The CID of *m/z* 149 contained two major ions at *m/z* 91 and *m/z* 119 due to $[C_2H_3SO_2]^+$ and $[C_4H_7SO_2]^+$, respectively, with a relative intensity ratio of 100:99 (Figure 10b). The proposed fragmentation pathway is illustrated in Scheme 9.

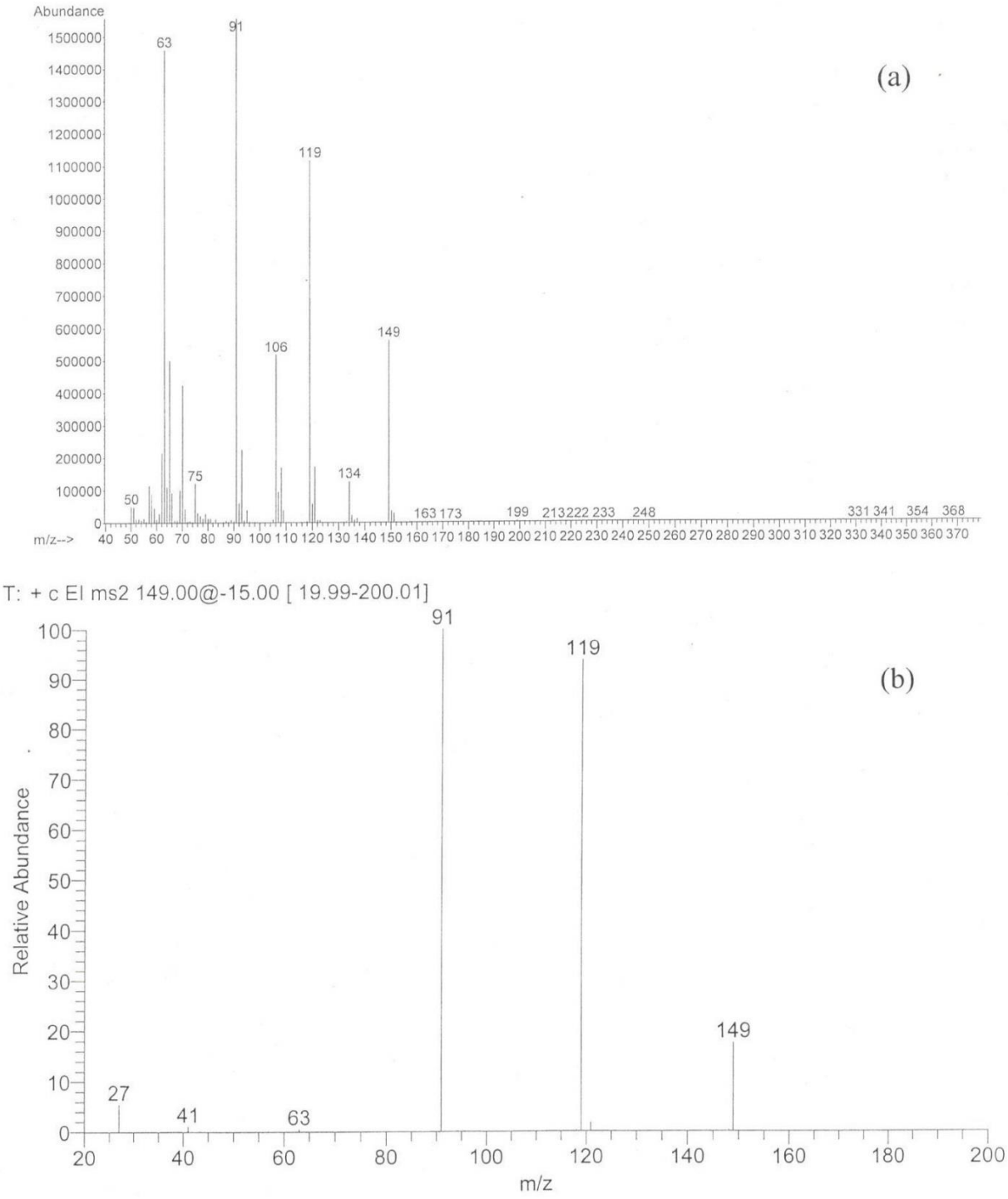
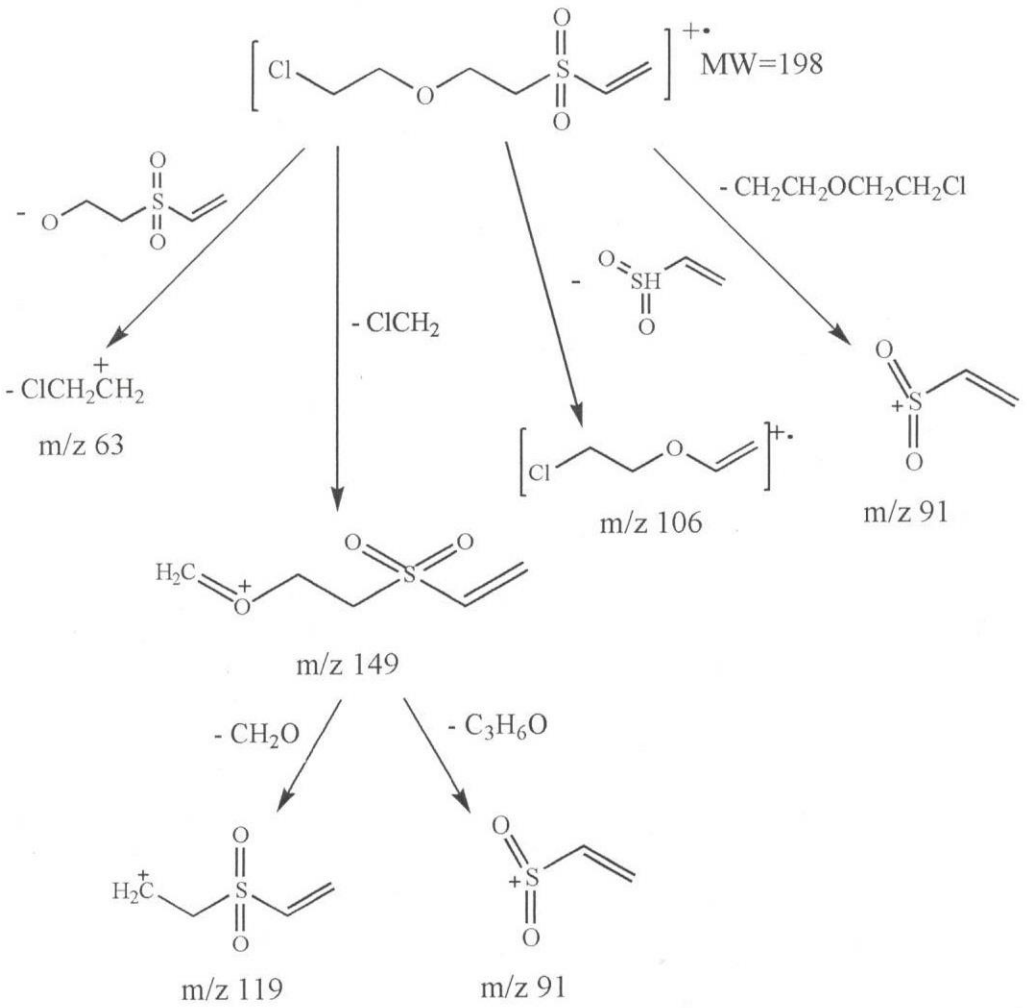


Figure 10. Mass spectra for compound **9**: (a) EI and (b) CID at *m/z* 149.



Scheme 9. Proposed fragmentation pathway for compound **9**.

The EI mass spectrum for compound **10** contained an extremely small to undetectable molecular ion at *m/z* 198 and a prominent mass ion at *m/z* 119 that formed due to $[M–OCH_2CH_2Cl]^+$. Lower mass ions at *m/z* 103 and *m/z* 59 were formed due to $[M–OCH_3\text{-}ClCH_2]^+$ and $[M–C_3H_8O–OCH_2CH_2Cl]^+$, respectively (Figure 11a). The CID of *m/z* 119 contained two major ions at *m/z* 59 and *m/z* 87 due to $[C_2H_3S]^+$ and $[C_4H_7S]^+$, respectively, with a relative intensity ratio of 100:11 (Figure 11b). The proposed fragmentation pathway is illustrated in Scheme 10.

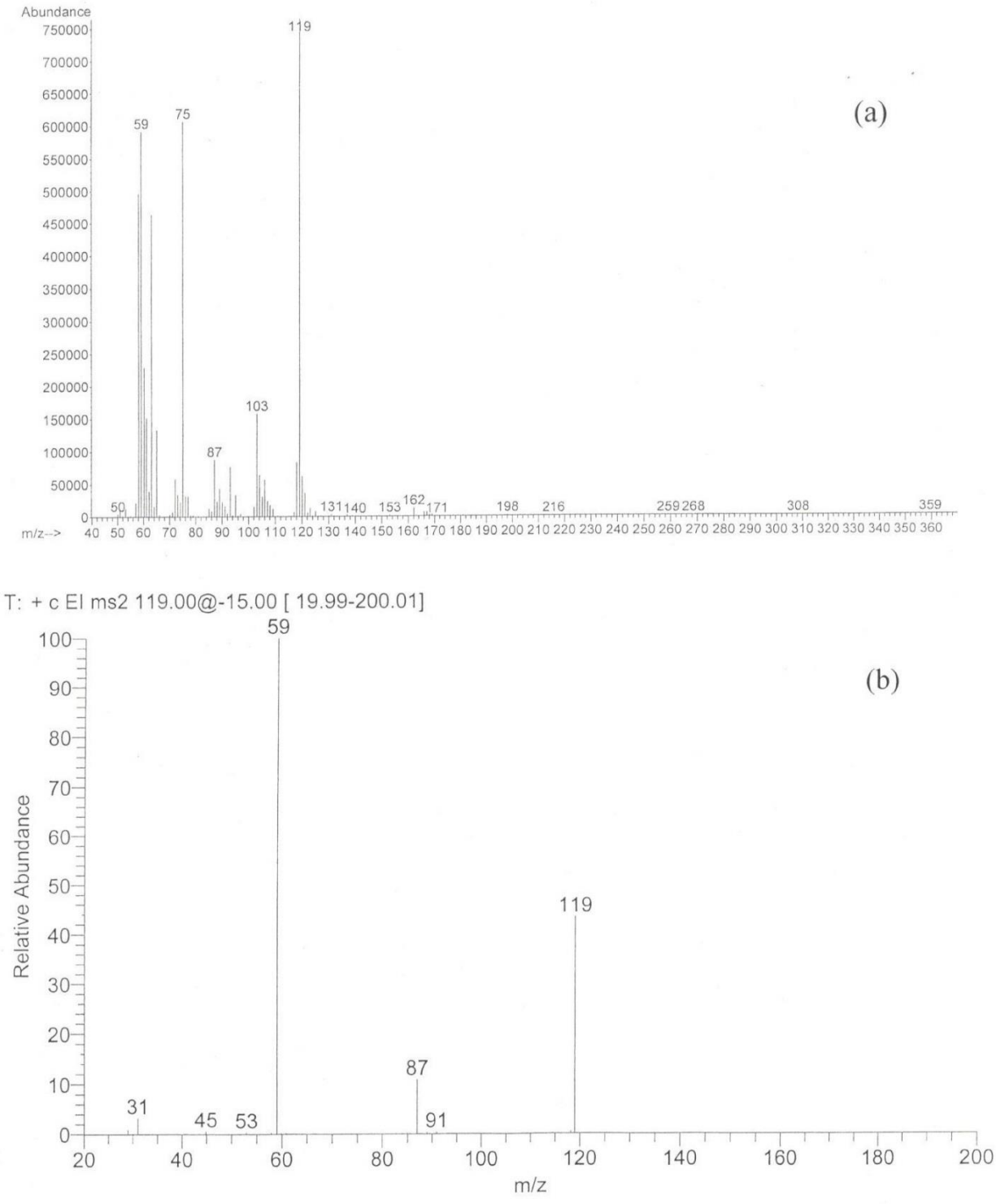
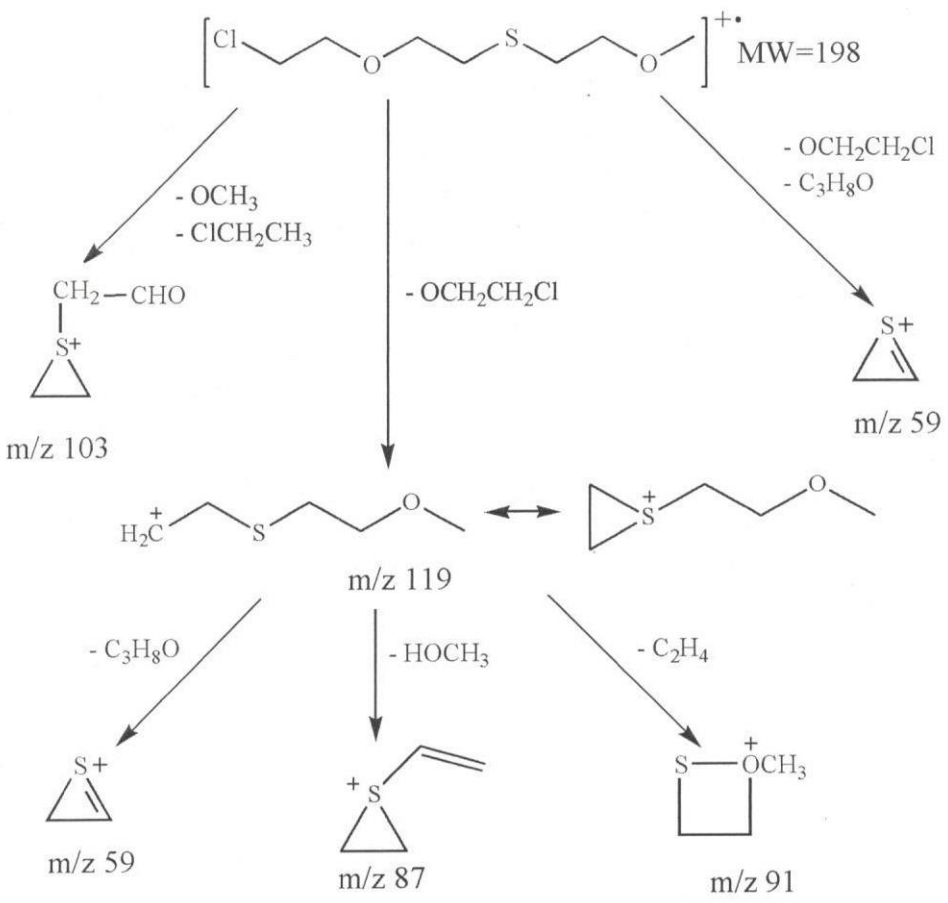


Figure 11. Mass spectra for compound **10**: (a) EI and (b) CID at *m/z* 119.



Scheme 10. Proposed fragmentation pathway for compound **10**.

The EI mass spectrum for compound **11** did not show a molecular ion at *m/z* 212. The higher mass ion at *m/z* 167 was formed due to $[M–OCH_2CH_3]^+$. The mass ion at *m/z* 133 that formed due to $[M–OCH_2CH_2Cl]^+$ could have been from one of two resonance structures shown in Figure 12a. The CID of *m/z* 133 contained four major products: ions at *m/z* 45, *m/z* 73, *m/z* 87, and *m/z* 105, due to $[C_2H_5O]^+$, $[C_4H_9O]^+$, $[C_4H_7S]^+$, and $[C_4H_9SO]^+$, respectively, with a relative intensity ratio of 98:100:7:6 (Figure 12b). The full proposed fragmentation pathway is illustrated in Scheme 11.

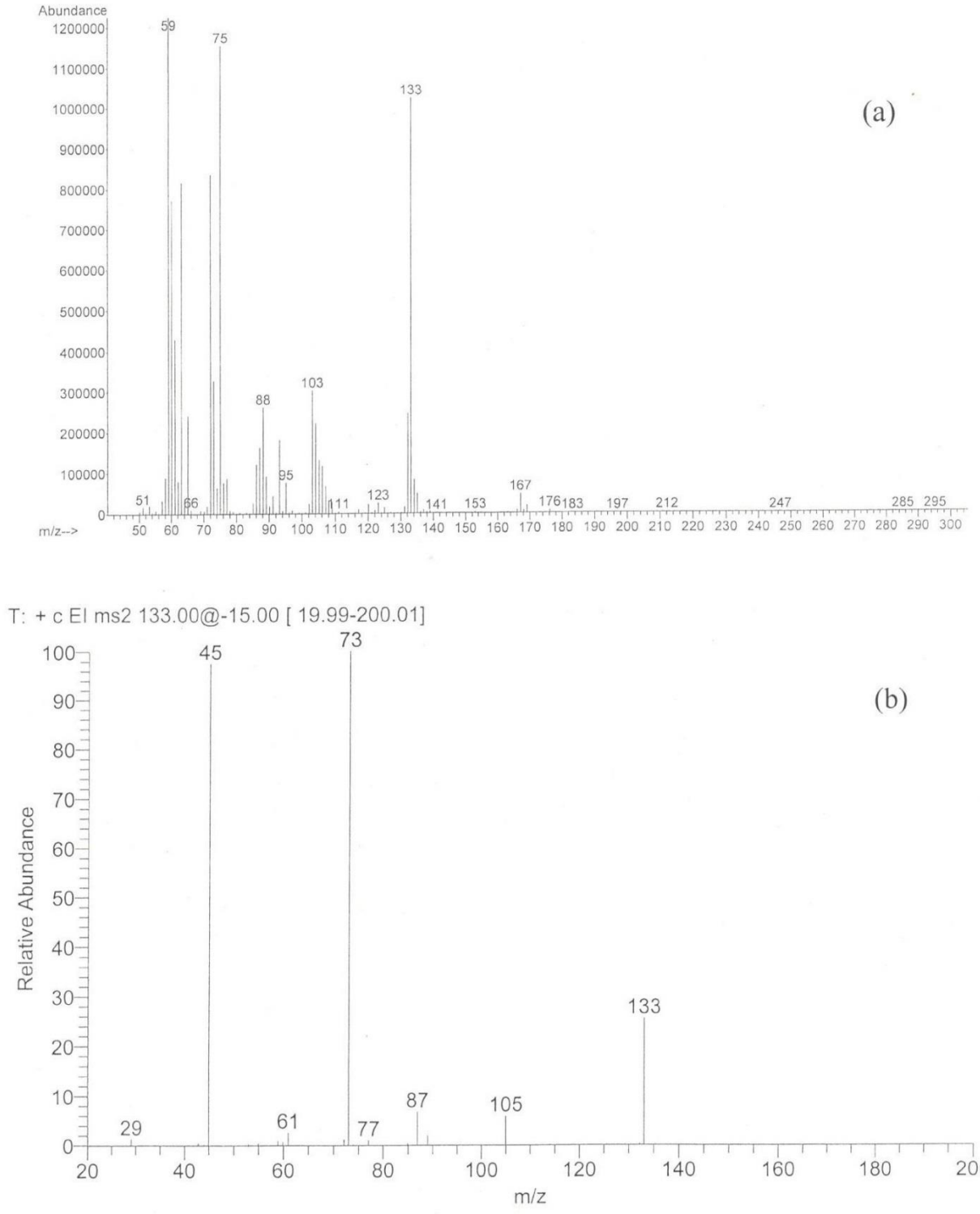
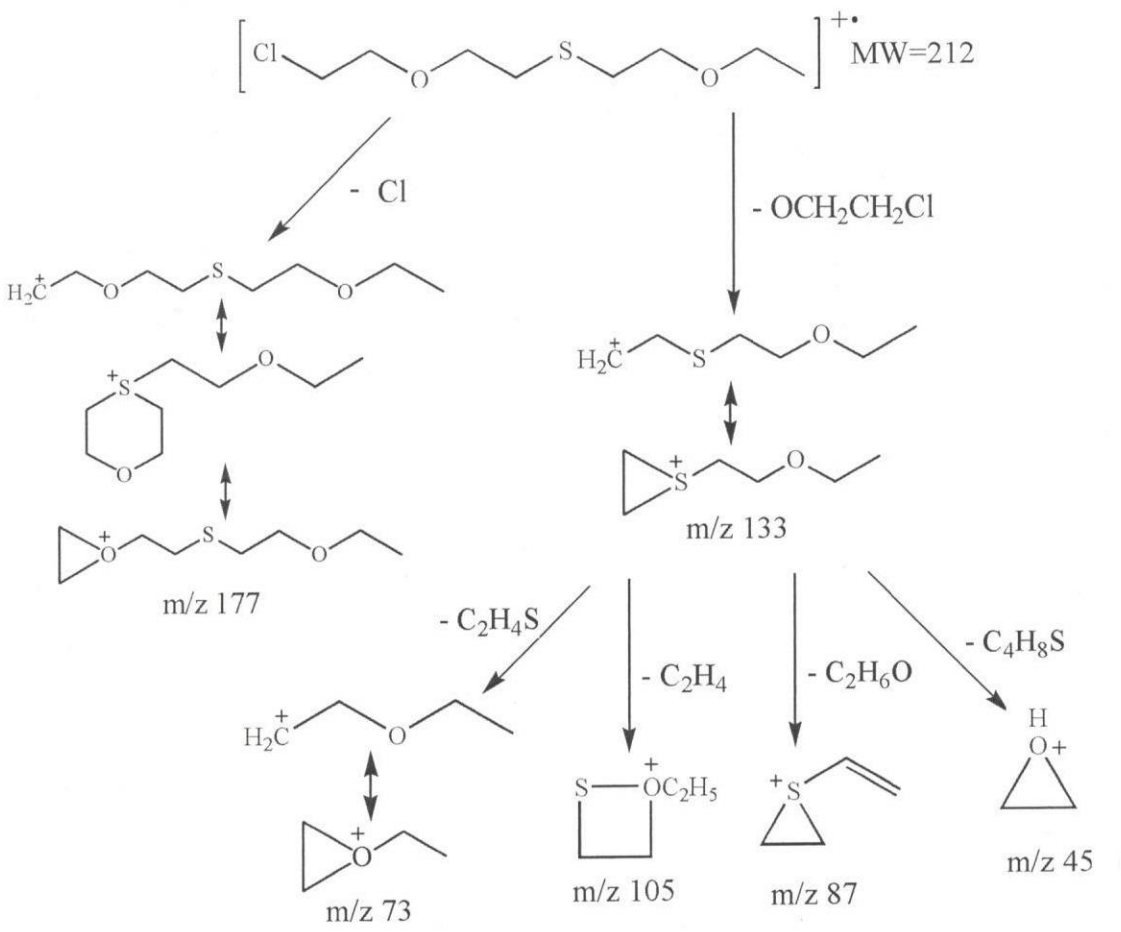


Figure 12. Mass spectra for compound **11**: (a) EI and (b) CID at *m/z* 133.



Scheme 11. Proposed fragmentation pathway for compound **11**.

The fragmentation pathway for the sulfide-group-containing molecules (**1**, **4**, **7**, **10,** and **11**) undergoes a β-carbon cleavage due to the nucleophilicity of sulfur, followed by elimination of a leaving group (OH^-, Cl^-, OMe^-, and OEt^-). For compound **7**, the sulfur was less nucleophilic because of the vinyl sulfide; thus, the metastable ion formation occurred at sites (a) and (b) in Figure 13.

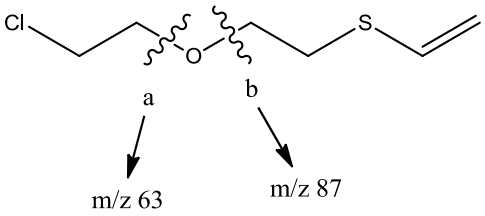


Figure 13. Fragmentation of vinyl sulfide **7**.

The fragmentation pattern of the sulfoxide-group-containing molecules (**2**, **5,** and **8**) could generally be rationalized to M–$SO^{24–26}$ (first α-carbon cleavage) to form an *m/z* 107 ion (Figure 14), followed by loss of C_2H_3Cl to form an *m/z* 45 ion and loss of C_2H_4O to form an *m/z* 63 ion for all three compounds.

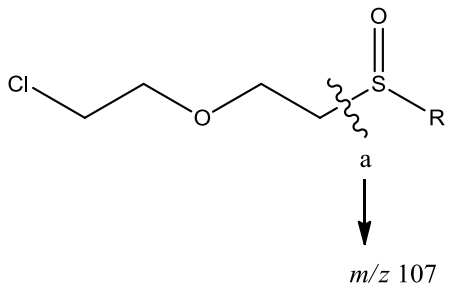


Figure 14. Initial fragmentation of sulfoxides (**2**, **5,** and **8**).

For the sulfones (**3**, **6,** and **9**), the fragmentation pathway undergoes M–SO_2, as shown in Figure 15: the loss of CH_2Cl (a) occurred first and was followed by the loss of CH_2O (b). The ring formation (*m/z* 93) was observed for **3** and **6** due to the leaving group at the β-carbon position. Compound **9** had a vinyl group preventing the formation of a ring structure; thus, an ion at *m/z* 91 was observed.

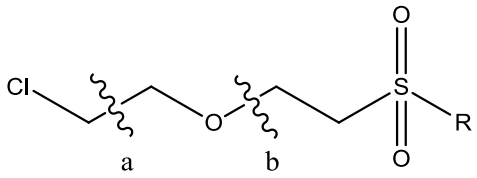


Figure 15. Fragmentation of sulfones (**3**, **6,** and **9**).

4. CONCLUSION

GC–MS was used to analyze 1-(2-chloroethoxy)-2-[(2-chloroethyl)thio] ethane along with 10 related compounds. GC–QQQ was then used to obtain the CID mass spectra for other ions of interest to further confirm fragmentation. The results illustrate a tandem mass spectrometric approach for the confirmation of sulfur mustard degradation products and associated compounds. Because of their ruggedness, modern GC–MS instruments are the most common analytical tools for investigations of potential mustard use in the field. The findings in this report will add to the spectral reference library of mustard-related compounds in the chemical weapons community.

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ACRONYMS AND ABBREVIATIONS

CID	collision-induced dissociation
CWC	Chemical Weapons Convention
EI	electron impact
GC	gas chromatography
MS	mass spectrometry
MS-MS	tandem mass spectrometry
QQQ	triple-quadrupole mass spectrometry

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